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## Ultranonlocality in Time-Dependent Current-Density-Functional Theory: Application to Conjugated Polymers

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We solve the long-standing problem of the large overestimation of the static polarizability of conjugated polymers obtained using the local density approximation within density-functional theory. The local approximation is unable to describe the highly nonlocal exchange and correlation (xc) effects found in these quasi-one-dimensional systems. Time-dependent current-density-functional theory enables a local current description of ultranonlocal xc effects using the Vignale-Kohn functional [G. Vignale and W. Kohn, *Phys. Rev. Lett.* **77**, 2037 (1996)]. Except for the model hydrogen chain, our results are in excellent agreement with the best available correlated methods.

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Time-dependent density-functional theory (TDDFT) [1–3] is a promising method for calculating properties of many-electron systems. The method can handle large systems and is, in principle, exact. So far TDDFT has been applied mainly within the adiabatic local density approximation (ALDA) in which the exchange-correlation (xc) potential is a local functional of the electron density. For many properties this approximation leads to results which are competitive in accuracy with other advanced many-body methods, but was shown to fail dramatically for long molecular chains. For this case large overestimations of the axial polarizabilities and hyperpolarizabilities were observed [4]. The reason for the failure of the ALDA is precisely its locality. Since it depends only on the local density, the ALDA potential in the center of the molecular chain is insensitive to changes in the charges at the end points of the chain that are induced by an external field. This is also true for gradient corrected potentials. For the exact potential, however, the induced end point charges turn out to have important global effects. They give rise to a counteracting potential that increases linearly along the molecular chain [4,5]. Such a counteracting term cannot be reproduced by a simple local density approximation, which causes the overestimations of the polarizabilities in the ALDA. To describe the global changes in the potential in terms of the electron density, the functional must be ultranonlocal [5].

It was pointed out by Vignale and Kohn (VK) [6,7] that a local approximation can still be used if the basic variable is the induced current density rather than the density. Their original motivation was to develop an xc functional that is nonlocal in time, but still local in space. It was found that nonlocality in time implies ultranonlocality in space, if one insists on using the density as a basic variable. However, a dynamical xc functional that is nonlocal in time, but local in space, can be constructed in terms of the current. As the current density in the bulk of the system measures the charge buildup at the boundaries, it can be used as a local

indicator of global changes in the system. The variable conjugate to the current is the vector potential. In time-dependent current-density-functional theory (TDCDFT) this vector potential also has an xc component, which is simply related to the xc electric field. VK derived an explicit expression for this xc field, which has already been applied successfully to plasmon linewidths in quantum wells [8] and in a simplified form to optical spectra of solids [9]. VK did a careful analysis of the weakly inhomogeneous electron gas and arrived at the following equation [6,7,10] for the induced xc-electric field, which we write in the form of a viscoelastic field derived by Vignale, Ullrich, and Conti [11]:

$$\delta \mathbf{E}_{xc} = \nabla \delta v_{xc}^{ALDA} + i\omega \delta \mathbf{A}_{xc}^{viscoel}, \quad (1)$$

$$\delta A_{xc,i}^{viscoel} = \frac{i}{\omega n_0(\mathbf{r})} \sum_j \partial_j \sigma_{xc,ij}(\mathbf{r}, \omega), \quad (2)$$

where  $\sigma_{xc,ij}$  has the structure of an isotropic viscoelastic stress tensor

$$\sigma_{xc,ij} = \tilde{\eta}_{xc}(\partial_j u_i + \partial_i u_j - \frac{2}{3} \delta_{ij} \nabla \cdot \mathbf{u}) + \tilde{\zeta}_{xc} \delta_{ij} \nabla \cdot \mathbf{u}. \quad (3)$$

Here  $\mathbf{u}(\mathbf{r}, \omega) = \delta \mathbf{j}(\mathbf{r}, \omega)/n_0(\mathbf{r})$  is the velocity field,  $\delta \mathbf{j}(\mathbf{r}, \omega)$  the induced current, and  $n_0(\mathbf{r})$  the ground state density. The coefficients  $\tilde{\eta}_{xc}(n_0(\mathbf{r}), \omega)$  and  $\tilde{\zeta}_{xc}(n_0(\mathbf{r}), \omega)$  are frequency dependent functions of the ground state density and represent complex bulk and shear viscosities. They are determined by the longitudinal and transverse response kernels  $f_{xcL}(n_0, \omega)$  and  $f_{xcT}(n_0, \omega)$  of the homogeneous electron gas according to [11]

$$\tilde{\eta}_{xc} = -\frac{n_0^2}{i\omega} f_{xcT}, \quad (4)$$

$$\tilde{\zeta}_{xc} = -\frac{n_0^2}{i\omega} \left( f_{xcL} - \frac{4}{3} f_{xcT} - \frac{d^2 \epsilon_{xc}}{dn_0^2} \right), \quad (5)$$

where  $\epsilon_{xc}(n_0)$  is the xc energy per unit volume of the homogeneous electron gas of density  $n_0$ . The transverse

kernel appears because, in general, we will not only have longitudinal currents but also transverse ones. Equation (3) is analogous to an expression which describes forces in an elastic medium, in which case  $\mathbf{u}$  is a displacement field.

The VK functional was derived by an expansion to second order in wave vectors  $k$  and  $q$  which characterize the Fourier component of the current-current response function and the wavelength of the inhomogeneity, respectively. Since the expansion was carried out to second order, we need only second derivatives of the current in real space. This expansion was shown to be valid in the regime  $k, q \ll k_F, \omega/v_F$  where  $k_F$  and  $v_F$  are the Fermi momentum and velocity. This is the region above the particle-hole continuum. However, the VK functional satisfies two important constraints which are valid for systems with arbitrary time dependence and inhomogeneity (such as molecules in external fields), stating that in linear response the xc-electric field does not exert any forces or torques on the system. Another exact property, which is satisfied for any system, is that under rigid translation of the center of mass, described by position vector  $\mathbf{x}(\omega)$ , the xc-potential is also translated over this vector. This immediately implies that the VK functional satisfies the so-called harmonic potential theorem [12,13].

In view of these exact properties one may wonder if the VK functional is applicable to systems such as molecules. Let us therefore check the constraints. For the wave vector of the applied optical field the constraints  $k \ll k_F, \omega/v_F$  are trivially met as  $k = \omega/c \ll k_F$  and the speed of light  $c \gg v_F$ . For the inhomogeneity wave vector  $q = |\nabla n_0|/n_0$  the situation is less clear. In the valence region  $q \approx k_F$  and  $qv_F \approx 1$ , whereas in the asymptotic outer region  $q \gg k_F$  and  $qv_F \ll 1$ . We should point out, however, that for finite systems, like molecules, the essential response features do not change much with frequency below the excitation gap  $\omega_{\text{gap}}$ . If we take this  $\omega_{\text{gap}}$  as the characteristic frequency, then both constraints are not strongly violated in the outer valence region. With this in mind, calculations on molecules can be performed at finite  $\omega$  and extrapolated to zero frequency (as is also done in experiment). Moreover, it should be noted that the particle-hole regime, for which the VK derivation is not justified, is to a large extent taken into account by the explicit evaluation of the Kohn-Sham response functions. In view of these arguments and the importance of the field of polymer physics, we considered it worthwhile to explore the merits of the VK functional for these systems. As we will show, the VK functional yields excellent results for these systems.

In TDCDFT we solve the following coupled set of self-consistent equations:

$$\delta n = \chi_{nj} \cdot \delta \mathbf{A}_{\text{eff}} + \chi_{nn} \cdot \delta v_{\text{eff}}, \quad (6)$$

$$\delta \mathbf{j} = \chi_{jj} \cdot \delta \mathbf{A}_{\text{eff}} + \chi_{jn} \cdot \delta v_{\text{eff}}, \quad (7)$$

where  $\chi_{nn}, \chi_{nj}, \chi_{jn}$ , and  $\chi_{jj}$  are the Kohn-Sham response functions. Here the product implies integration over spa-

tial coordinates. We define the gauge

$$\delta \mathbf{A}_{\text{eff}} = \delta \mathbf{A}_{\text{ext}} + \delta \mathbf{A}_{\text{xc}}^{\text{viscoel}}, \quad (8)$$

$$\delta v_{\text{eff}} = \delta v_H + \delta v_{\text{xc}}^{\text{ALDA}}, \quad (9)$$

where  $\delta \mathbf{A}_{\text{ext}}$  is the vector potential of the external electric field  $\mathbf{E}_{\text{ext}} = i\omega \mathbf{A}_{\text{ext}}$  and the  $\delta \mathbf{A}_{\text{xc}}$  is given in terms of the viscoelastic tensor of Eq. (2). Here  $\delta v_H$  represents the first order change in the Hartree potential and  $\delta v_{\text{xc}}^{\text{ALDA}}$  is the ALDA xc potential.

To implement the VK functional we need to evaluate the matrix elements  $H_{ia}(\omega)$  of the operator  $\hat{\mathbf{j}} \cdot \delta \mathbf{A}_{\text{xc}}^{\text{viscoel}}$  between occupied (i) and virtual (a) states, where  $\hat{\mathbf{j}}$  is the operator for the paramagnetic current. Integration by parts transfers the derivatives to the coefficients  $\tilde{\eta}_{\text{xc}}$  and  $\tilde{\zeta}_{\text{xc}}$ , and reduces the derivatives of the wave functions to first order. One arrives at two contributions,  $H_{ia} = H_{ia}^{\eta} + H_{ia}^{\zeta}$ , that are linear in, respectively,  $\tilde{\eta}_{\text{xc}}$  and  $\tilde{\zeta}_{\text{xc}}$ . Vignale, Ullrich, and Conti have shown [11] that  $\omega \tilde{\zeta}_{\text{xc}}(\omega)$  vanishes in the limit  $\omega \rightarrow 0$ , whereas only the imaginary part of  $\omega \tilde{\eta}_{\text{xc}}(\omega)$  remains finite in this limit. Therefore only  $H_{ia}^{\eta}$  contributes to the static polarizability. The strange fact that the shear modulus does not vanish in the limit of  $\omega \rightarrow 0$  (unlike in ordinary liquids) comes ultimately from the fact that the limit  $k \rightarrow 0$  is taken before the limit  $\omega \rightarrow 0$  (i.e., above the particle-hole continuum). Thus the system remains “dynamical” down to zero frequency. By contrast, the bulk modulus is already entirely accounted for by the ALDA.

This method has been implemented in the Amsterdam Density Functional (ADF) program [14]. The coefficients  $\tilde{\eta}_{\text{xc}}$  and  $\tilde{\zeta}_{\text{xc}}$  are evaluated in the  $\omega \rightarrow 0$  limit, in which case they depend only on the transverse xc-kernel  $f_{\text{xcT}}$ . We used Eq. (19) (and the values of  $\mu_{\text{xc}}$  in Table I) of Ref. [15] to obtain values for  $f_{\text{xcT}}(n_0, \omega = 0)$  at arbitrary  $n_0$ , thereby using a cubic spline interpolation in the range 0–5 for the  $r_s$  values, in which we take into account the exactly known small  $r_s$  behavior [16].

We studied five systems for which the traditional TDDFT/ALDA method is known to fail. The choice of these systems was further guided by the availability of comparative accurate many-body results, as well as their chemical and physical importance [17]. We studied the model hydrogen chain ( $\text{H}_{2n}$ ) and the conjugated systems polyacetylene (PA), polydiacetylene (PDA), polyyne (PY), and polythiophene (PT). These systems differ in their degree of bond order and chemical composition. All calculations were performed using a triple zeta Slater-type basis augmented with two polarization functions, with the exception of thiophene oligomers where we used a double zeta basis and one polarization function. Cores were kept frozen (C 1s and S 2p). The oligomer geometries [18–24] used are depicted in the insets of Figs. 1–5, and are identical to the geometries of the reference work cited in the captions. Only for PT is our geometry slightly different.

In Fig. 1 we compare our VK and ALDA results for the static axial polarizability for PA with restricted

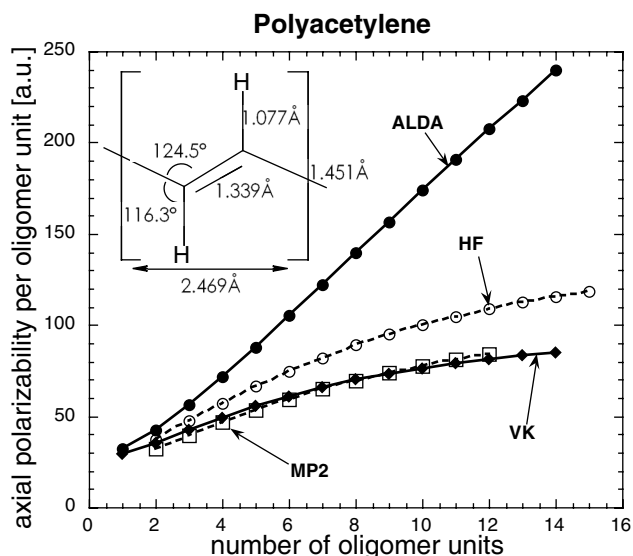


FIG. 1. ALDA and VK static axial polarizability of polyacetylene compared with restricted Hartree-Fock [18] and MP2 [22] results.

Hartree-Fock calculations [18], and second order perturbation theory (MP2) results [22]. We see that the VK functional gives a huge correction of the ALDA results. The VK results lie close to Hartree-Fock and are in excellent agreement with MP2. The results for the other conjugated molecules are shown in Figs. 2–4. In all cases we observe huge improvements of the results obtained with VK as compared to ALDA. They are in good agreement with the best available many-body results. The VK polarizabilities of PDA and PT lie below the Hartree-Fock results. In organic molecules containing mainly carbon and hydrogen atoms a trend can be observed in which the static

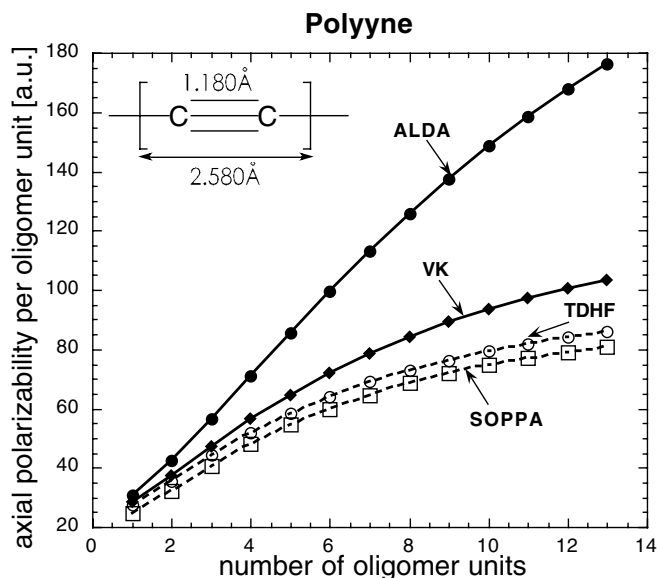


FIG. 3. ALDA and VK static axial polarizability of polyyne compared with time-dependent Hartree-Fock (TDHF) and second-order polarization propagator approximation (SOPPA) results [23].

polarizability decreases as one goes beyond the Hartree-Fock approximation [22–24]. This is in keeping with our results, with the exception of PY, where our results lie above the time-dependent Hartree-Fock as well as Green function results [20,23]. This may indicate that further improvements are needed in the functional.

For the model hydrogen chain, Fig. 5, we see only a slight improvement of VK over ALDA. In a conjugated system the induced current is carried by the  $\pi$  bonds which

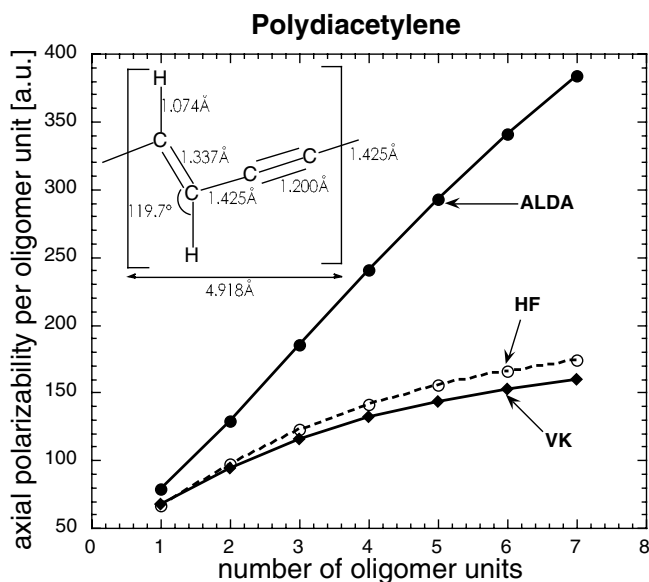


FIG. 2. ALDA and VK static axial polarizability of polydiacetylene compared with coupled Hartree-Fock results [19].

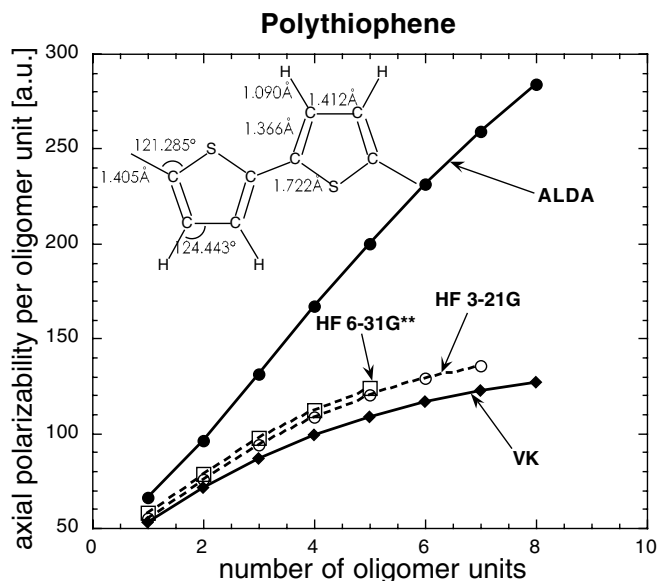


FIG. 4. ALDA and VK static axial polarizability of polythiophene compared with coupled perturbed Hartree-Fock results [21] using the 3-21G and 6-31G\*\* atomic basis sets.

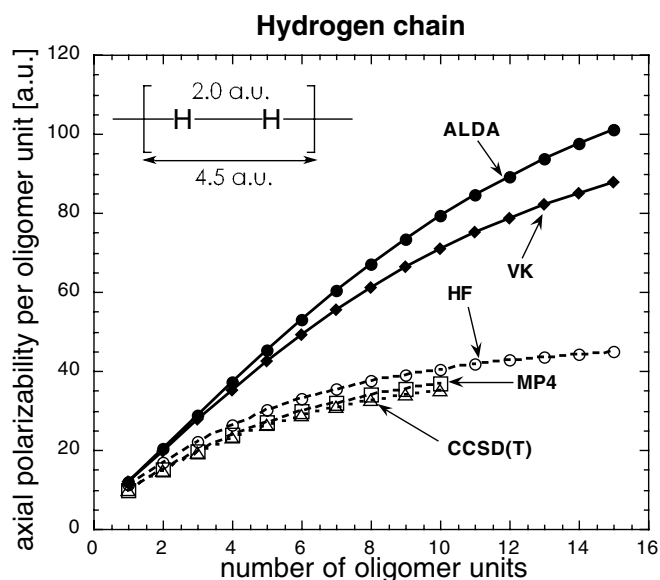


FIG. 5. ALDA and VK static axial polarizability of hydrogen chains compared with coupled Hartree-Fock (HF), MP4, and coupled cluster [CCSD(T)] results [24].

are delocalized over the entire molecule. In hydrogen, on the other hand, the dominant contributions arise from polarized  $\sigma$  bonds within the  $H_2$  units. For the two types of systems we therefore probe different density regions. The underestimation of the VK correction in the  $H_{2n}$  case may therefore be explained by an insufficient description of the density dependence of the transverse xc kernel.

In conclusion, we solve the long-standing problem of the large overestimation of the static polarizability for conjugated polymers by the local density approximation. This was achieved by using the Vignale-Kohn current functional in the framework of current density functional theory. In this theory the transverse xc kernel  $f_{xcT}$  plays a crucial role. Although in the model  $H_{2n}$  chains the improvement is small, for all conjugated polymers that we studied large improvements are found which bring our results close to the best available many-body results. More examples will be published in a forthcoming paper.

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